— 2004 IMF Review

Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations

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Richard D. Noble, Manuel Arruebo

Thomas M. Anderson

June 23, 2004

Sandia National Laboratories

GOODYEAR CHEMICAL

Burns & McDonnell SINCE 1898

Colorado University of Colorado at Boulder

Agenda

- Team Members
- Background
- Project
  - Description and Goals
  - Milestones
  - Funding
  - Benefits
- Technical
- Summary

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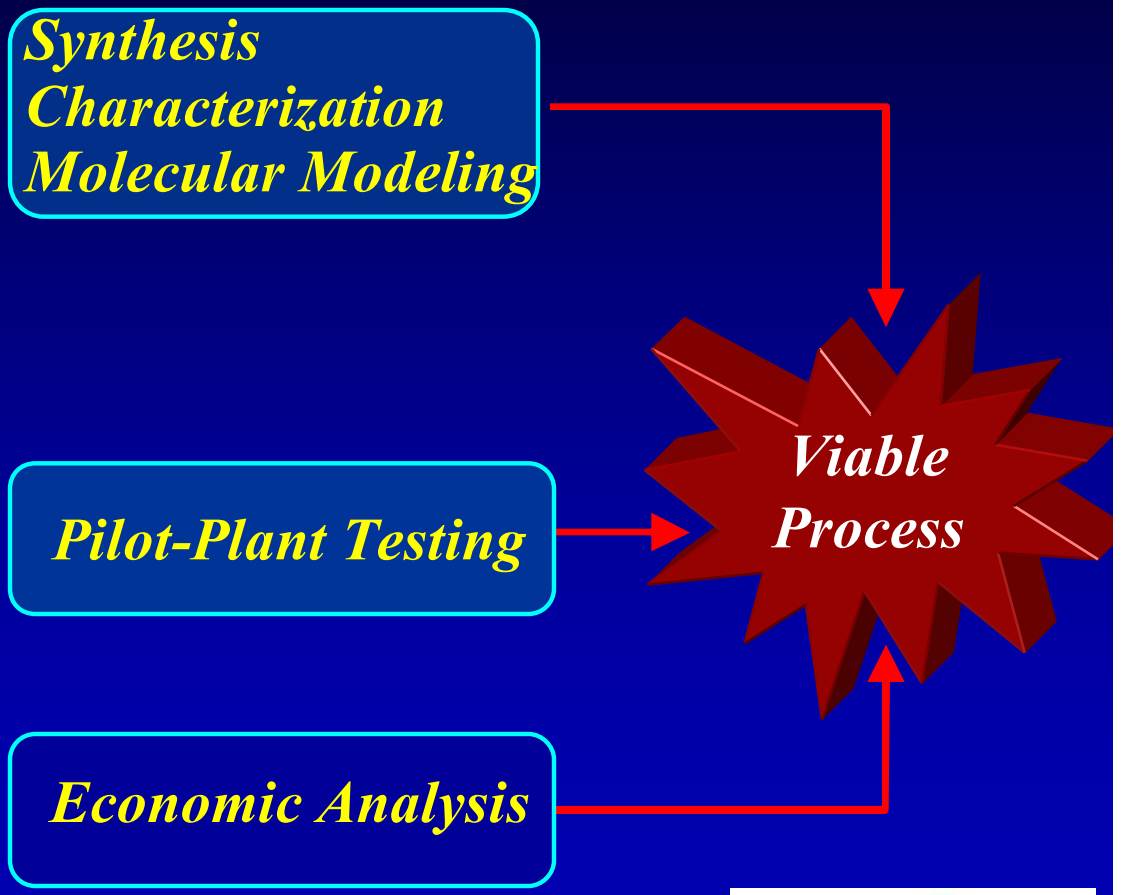
— Research Team

Sandia National Laboratories
Tina M. Nenoff
Mutlu Ulutagay-Kartin
Marcus G. Martin

University of Colorado
Richard D. Noble
Manuel Arruebo

Goodyear Chemical
Gary Gray

Burns & McDonnell
Tom Anderson



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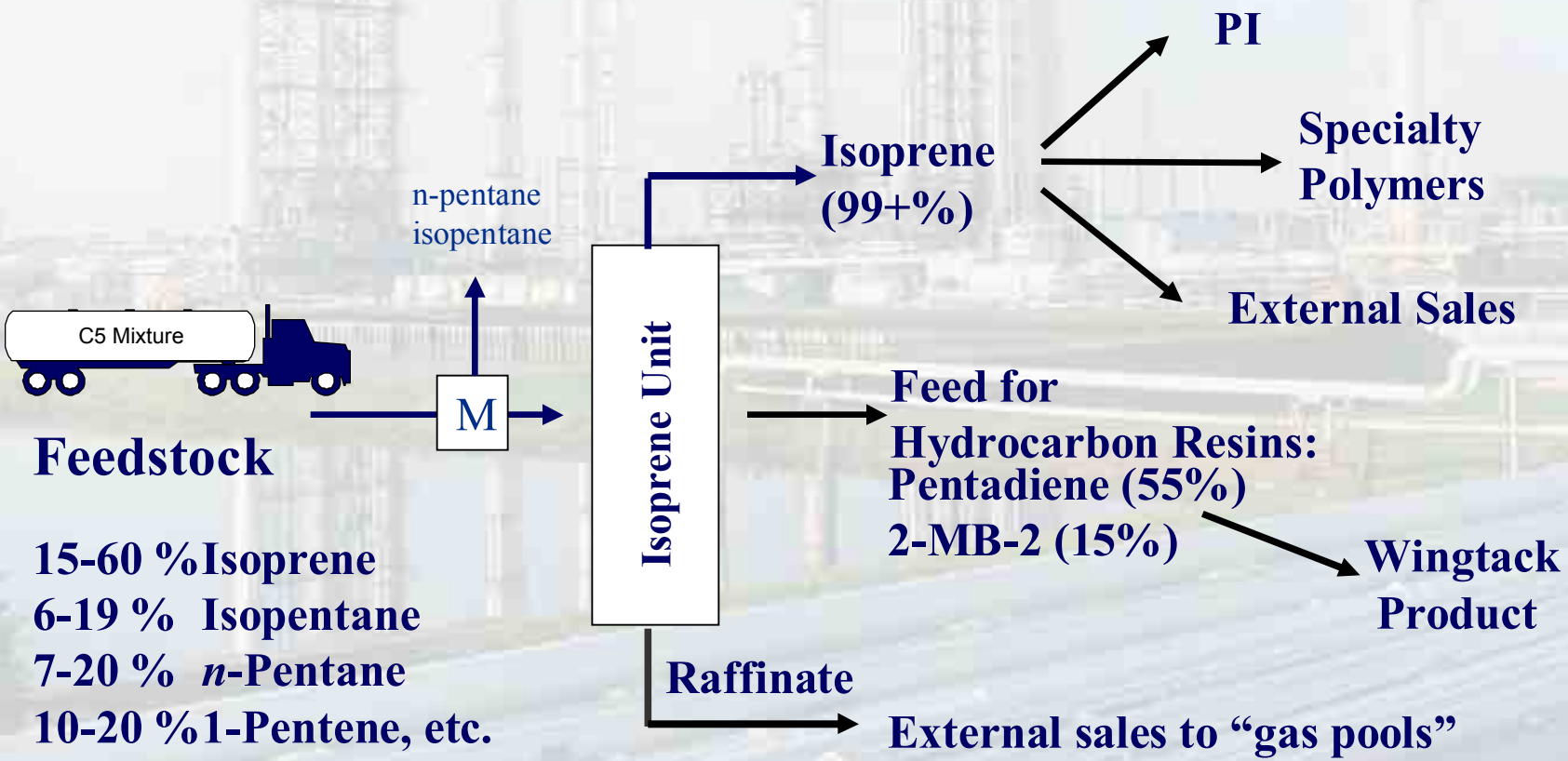
Background/Business Case

Objective: Reduced Energy Consumption Using Membranes

Proposed Isoprene Monomer Technology



Feedstock

15-60 % Isoprene
6-19 % Isopentane
7-20 % *n*-Pentane
10-20 % 1-Pentene, etc.

M = Membrane Location

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— DOE/IMF Project Description & Goals

Description

Create materials for Energy Efficient HC separations

- Scientific focus on surface modified zeolites
- Enrichment / separation of isoprene from C5 stream
- Separations to provide basis of application toward other energy-intensive C2-C5 separation processes

Goals

- Develop new membrane materials or separation-based adsorbents *via* modification of commercially-available zeolites
- Establish zeolite structure-property models for this technology & others
- Decrease energy consumption in the chemical & petroleum industries by employing these new & improved materials

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—Goodyear/Sandia/UC Project Milestones

Milestones

- ✓ Yr1: Zeolite Modification and testing; Go/No Go
  Initial Economic Analysis
- ✓ Yr2: Selection of "best" modified zeolite through characterization and testing; modification optimization
- Yr3: Pilot Plant testing, material modification;
  In-depth economic calculations;
  Engineering Analysis

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— DOE/OIT/IMF Project Funding

"Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations"

Collaborative Research

238K/yr OIT/IMF "Direct to SNL"
188K/yr Goodyear "In-Kind"
120K/16 mo. Univ, of Colorado via SNL
10K/yr Burns & McDonnell "In-Kind"

$1.3M / 3yr program (FY02-04)
50% "in-kind" industry funding,
commenced 4/23/2002.

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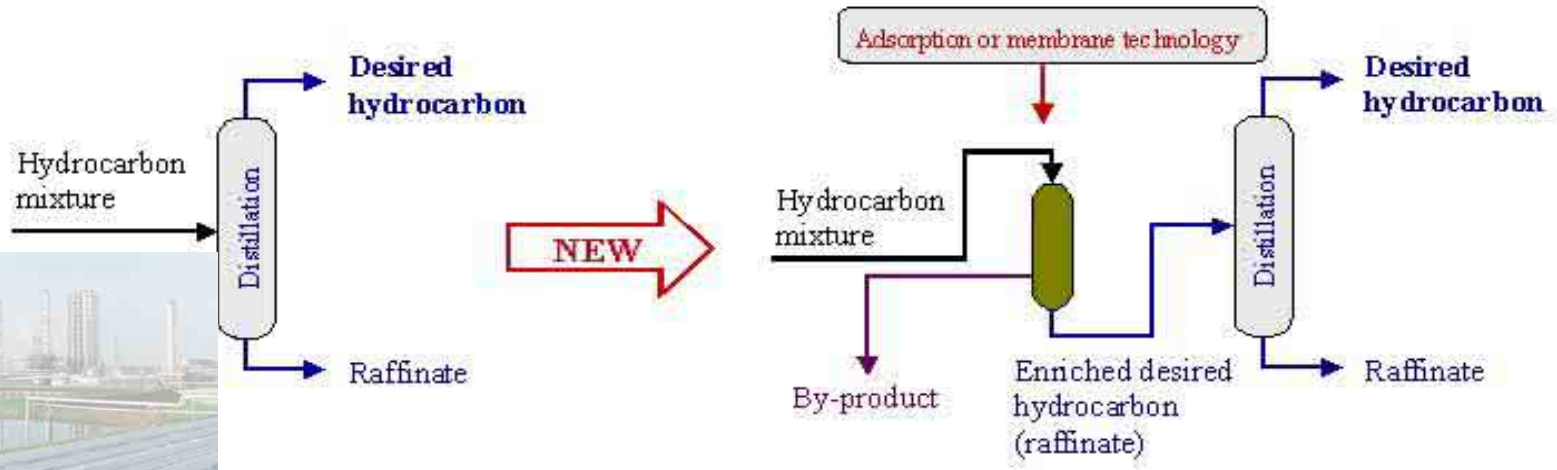
Potential Benefits to Goodyear: *Energy Savings*

Need: *Process Improvement for Isoprene Separation*

Current Technology	**Proposed Technology** Adsorption or Membrane Separation

12 % Reduction in Energy



Energy Intensive	**Less Energy Intensive**

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— Potential Energy Benefits to U.S. Chemical Industry

- Goodyear is the domestic leader in isoprene production (60%)
- Economic Modeling from Burns & McDonnell shows reduction (12%) in Goodyear's energy consumption using modified Zeolites (membranes)
- Extrapolation to C_2-C_5 industries predicts 39 Trillion BTU's savings

		Btu/yr., Trillion	2003 Billion lbs.	Btu/lb
Ethylene*-	C2	247	61	4,058
Propylene*-	C3	53	39	1,359
Butadiene*-	C4	27	5	5,366
(Isoprene-	C5		0.4	>6,000)
Total		327		

12 % Reduction

Source: CMR 2003 & DOE/OIT Energy & Environ. Profile 2002

** Btu/yr assumes cracking and distillation only. Associated downstream processes ignored*

GOODYEAR CHEMICAL

— Technical Section: Previous Technology Review

- Current technology - energy intensive fractional and extractive distillation
- Past patent literature shows the use of activated carbon/mole sieves technology* but does not have zeolite pore selectivity properties
- Other unmodified zeolite membranes rapidly deactivate from olefin & diolefin exposure

* US Patent Nos. 4,570,029, Kulprathipanja, S. , "Process for Separating Isoprene," 1986, UOP Inc.; 3,596,436 Dassese, P., Solvay & Cie.

— Technical Section: Separations Methodology

Sandia IP for Modified Zeolite Technology, combined leads to *enhanced* HC selectivity:

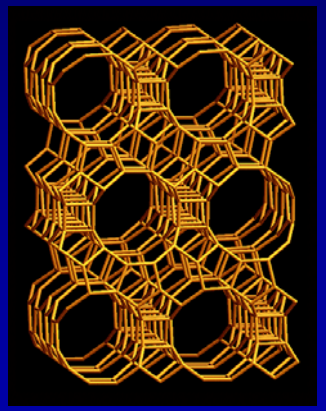
1) Molecular Sieving (pore size)

2) Adsorption Modification
(surface carbonization + acidity/reactivity)

3) Deactivation Stabilized
(high temp; multiple cycles)

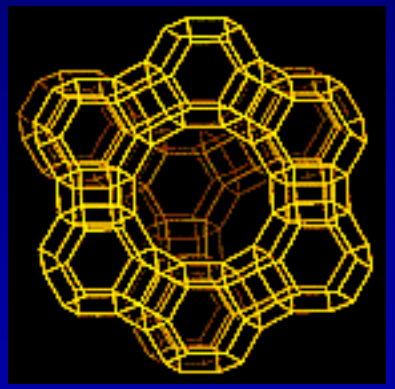
—Technical Section - Zeolites for Separations

	Relative acidity	Pore diameter (Å)
Zeolite β	high	6.6 x 7.7, 5.6
Zeolite-Y	medium-high	7.4
Zeolite-L	low	7.1
ZSM-5	high	5.1 x 5.5, 5.3 x 5.6



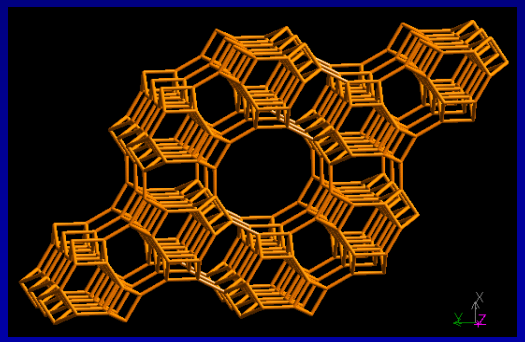
Zeolite-β

12 MR (3-D)
straight pores



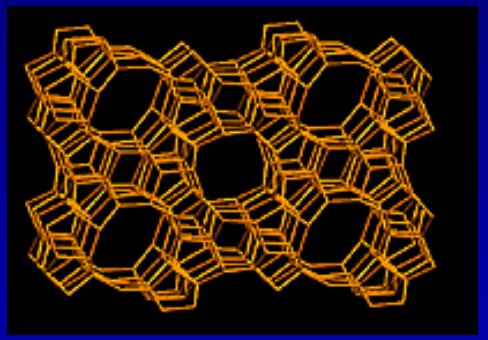
Zeolite-Y

12 MR (3-D, cages)
intersecting straight pores



Zeolite-L

12 MR (1-D)
straight pores



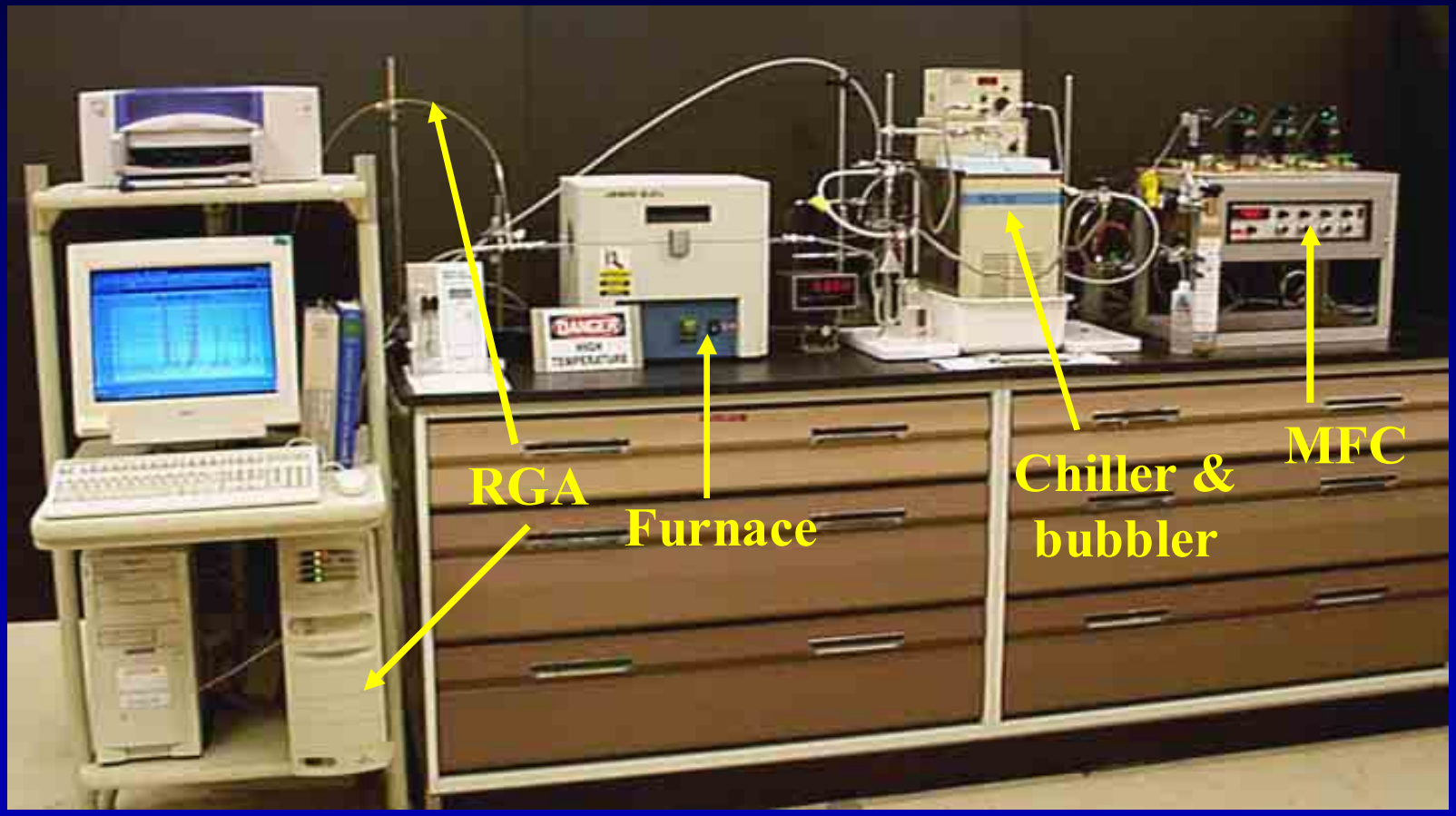
ZSM-5

10 MR (3-D)
Intersecting straight / sinusoidal pores

—Technical Section – General Approach for Synthesis and Modification of Zeolites

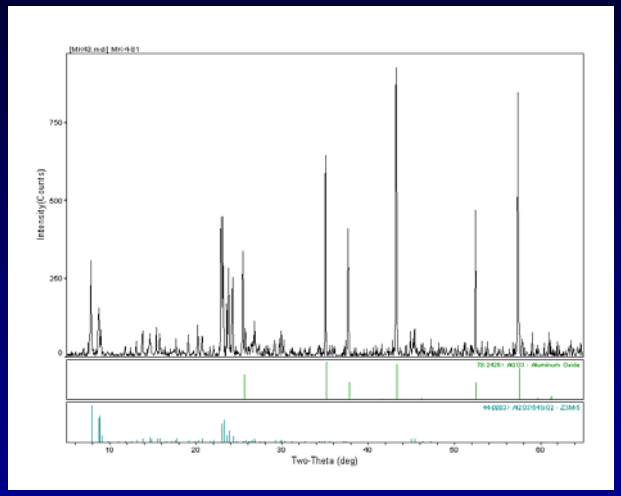
- ***Preparation of Zeolites:*** **The zeolite membranes are synthesized hydrothermally using the secondary (seeded) growth methods. The bulk zeolites are regenerated at high temperatures to remove ancillary pore-blocking molecules.**
- ***Bulk Carbonization:*** **The regenerated zeolites are carbonized w/hydrocarbons. The hydrocarbon type/mixture, concentration, flow rate, exposure time, and temperature are the variables for the modification process.**
- ***Characterization:*** **The effect of bulk carbonization on the pore size reduction and the adsorptivity of the zeolites are assessed with pore size measurements, *via* BET, and temperature-programmed desorption experiments, *via* NH_3-TPD, respectively.**
- ***Separation Experiments:*** **The carbonized zeolites and zeolite membranes are used for separation of n-pentane/i-pentane from a hydrocarbon C5 mixture at Goodyear.**

— Technical Section : In-house Sandia Reactor

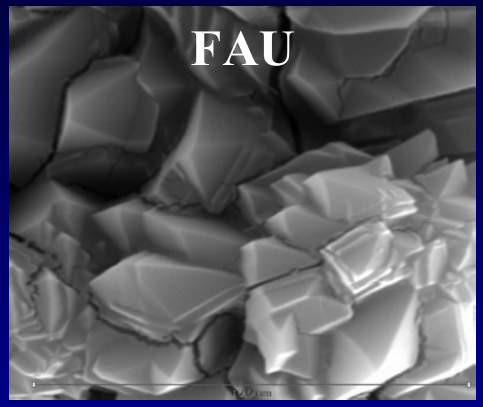


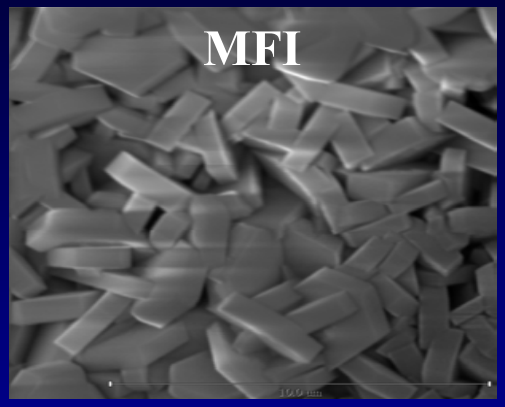
— Technical Section : Characterization Methods

PXRD

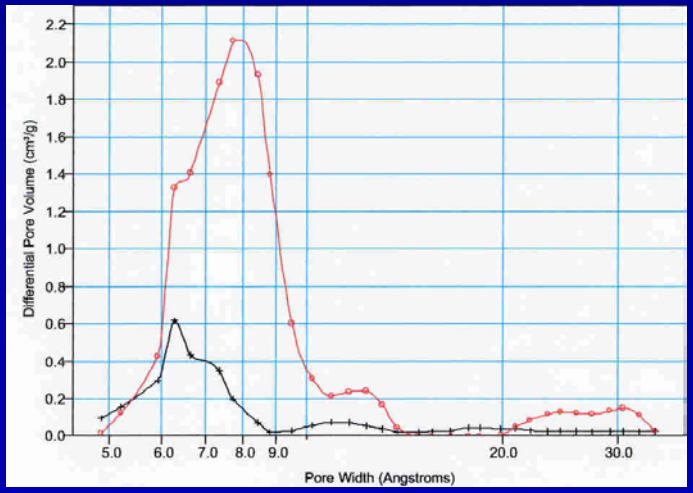


SEM

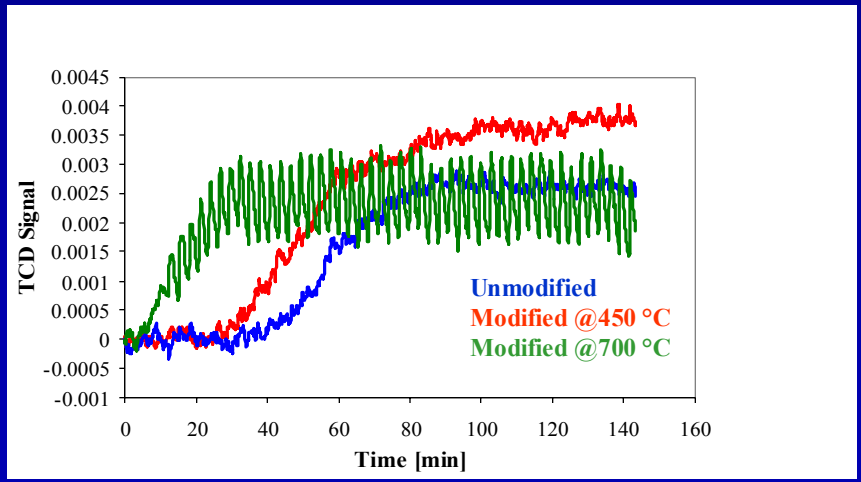




BET

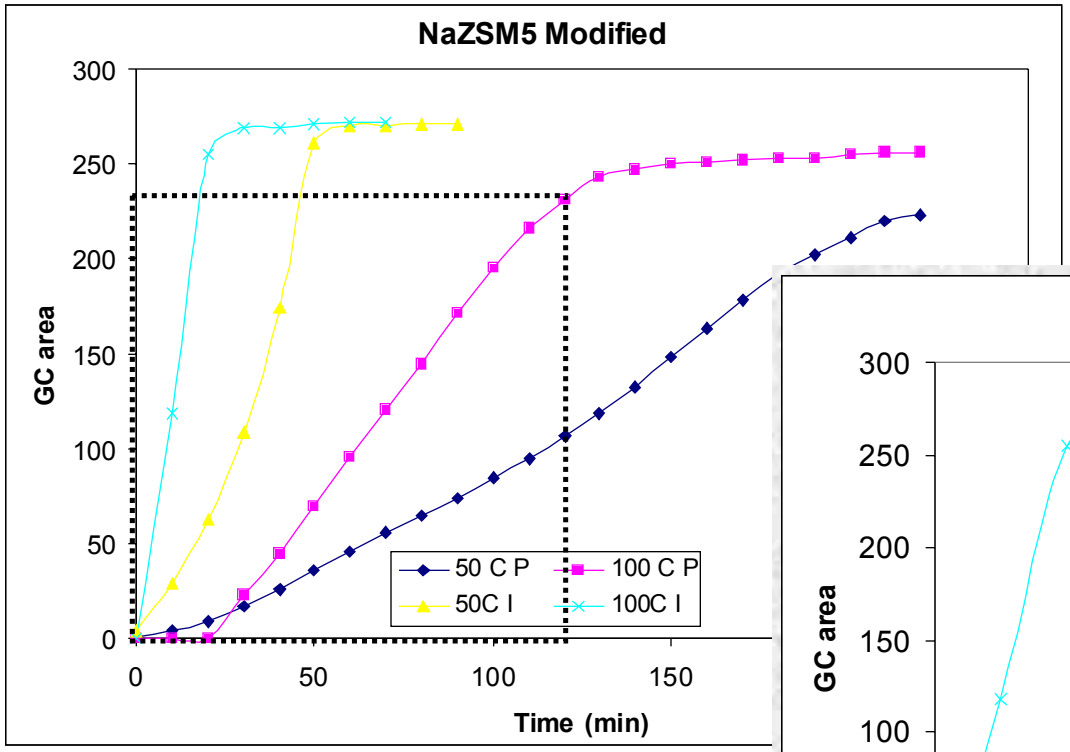


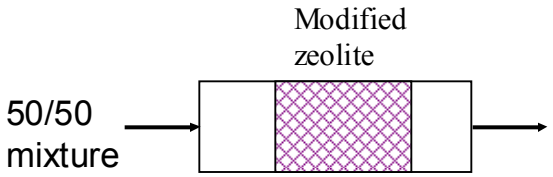
NH_3-TPD

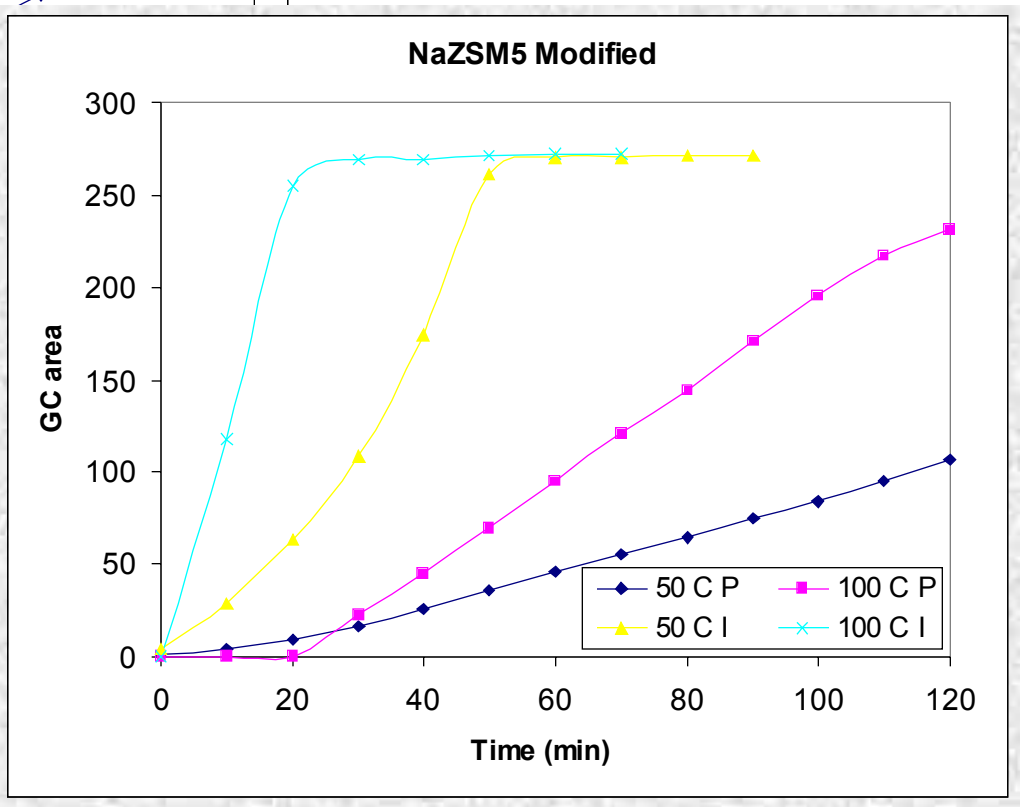


Technical Section : Bulk Experimental Results

screening experiments







Demonstrated isoprene/pentane separation using modified zeolite in dilute concentrations

Custom tailoring to preferentially adsorb pentane or isoprene

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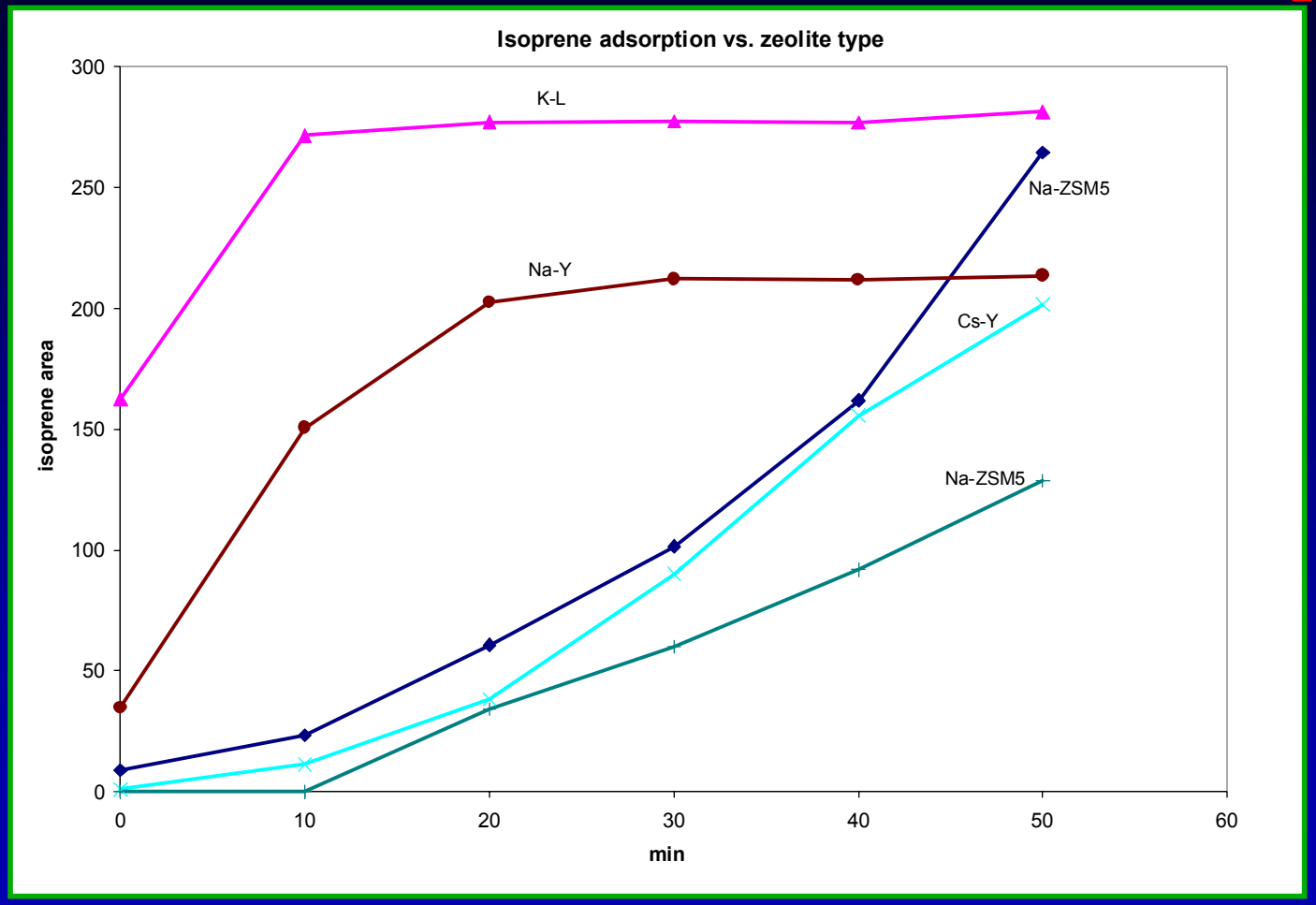
— Technical Section : Separation Results of Bulk Modified Zeolites at Room Temp.



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— Technical Section : Goodyear Separation Unit

MFC

Helium

Syringe Pump to
Feed Hydrocarbons

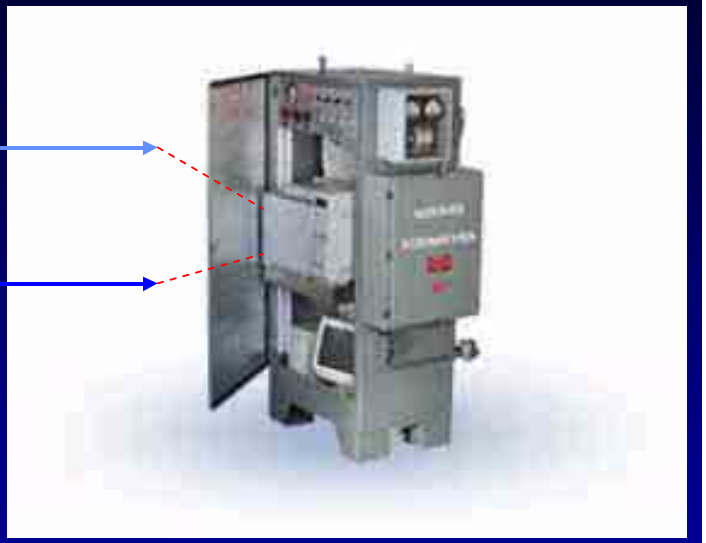
Zeolite
Membrane

Helium sweep

MFC

Permeate

Retentate



On-line GC

Separation Performance

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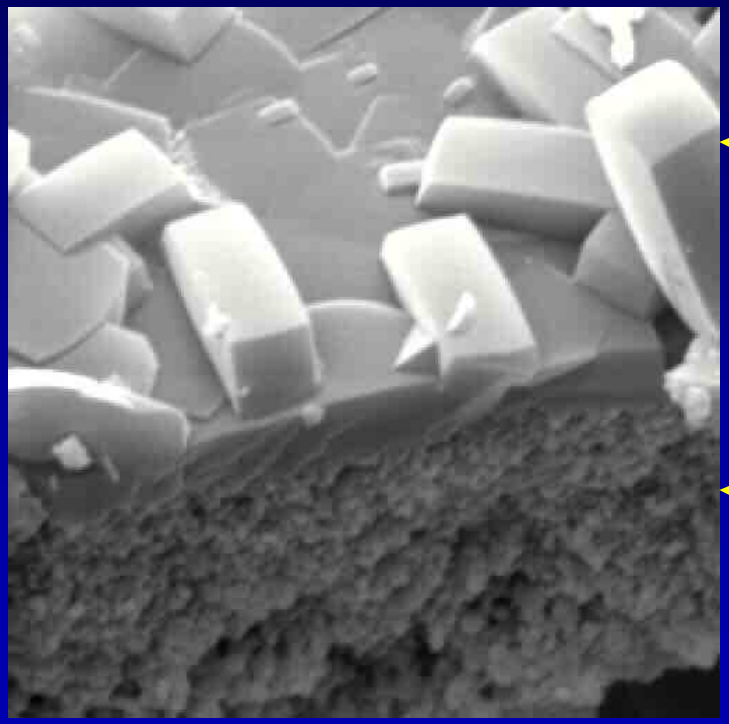
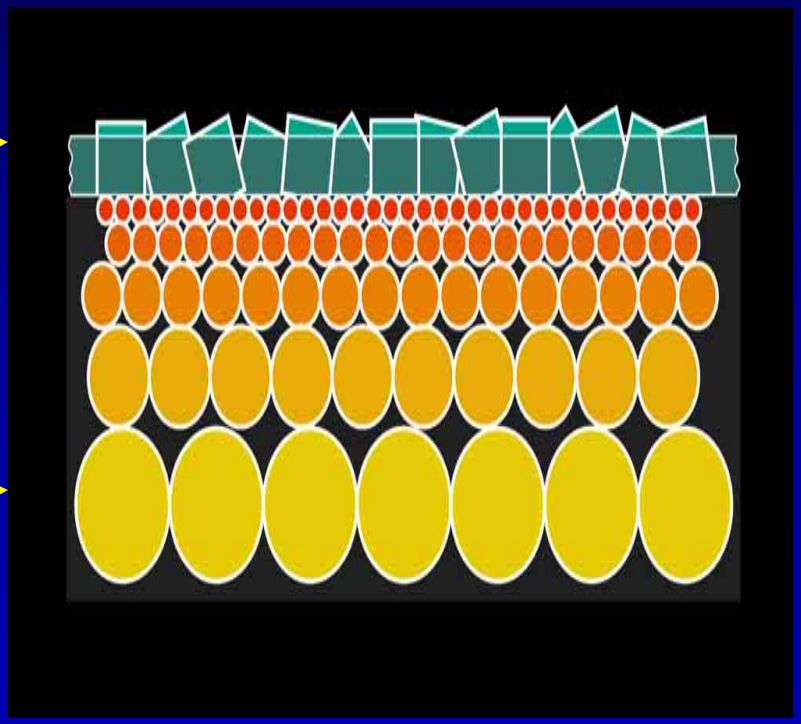
— Technical Section : Membrane Development

- *MFI and FAU type membranes have been produced*
- *Surface modification of the supported membranes are under way*

Crystalline Zeolite Membrane Layer (Selectively allows only specified Molecules to pass through)





Support (allows all molecules to pass)

— Technical Section : Economic Calculations Based on Membrane Separation Results

Separation Performance	% isoprene enrichment	% Energy Savings
Base	*0*	*0*
Demonstrated	0.6	1
Best case to date	3.0	6
Goal	6.7	12

Realistic and possible!

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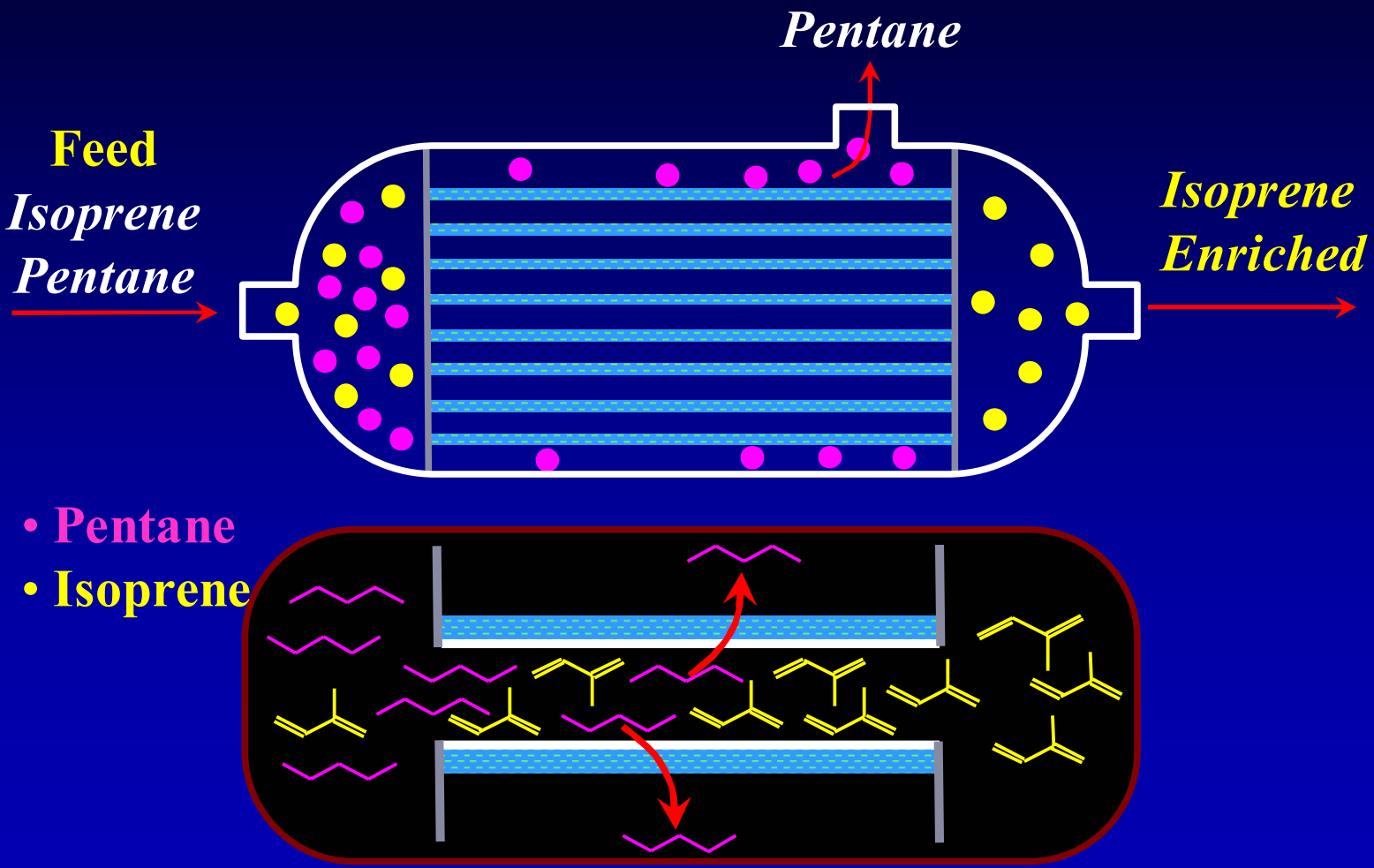
— Technical Section: Possible Module Design

Enhanced Selectivity: Molecular Sieving + Adsorption



— Summary : CRADA 1640.01 and IMF FY02

- New work to further enhance the fundamental knowledge and skills for isoprene purification for bulk and membranes
- Economic feasibility studies completed; point to attainable and realistic goals
- Bulk modification and adsorption studies plus initial membrane results show enrichment of isoprene from isoprene/pentane mixture
- Modification of of ZSM5 tubular supported membranes underway
- Additional industrial partner for commercialization (Pall Corp.) identified

Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94-AL85000.

Further Reading:

OFFICE OF INDUSTRIAL TECHNOLOGIES

http://www.oit.doe.gov/imf/factsheets/goodyr_zeolites.pdf